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Polyelectrolyte titration of whisky

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Abstract Polyelectrolyte titration using a fluorescent indicator was applied to determine the electrolytic charges in 10 whiskies at various pH levels. Tannic acid was also titrated to compare the relation between pH and charge because the polyelectrolytes in whisky were postulated to be polyphenols, mainly tannic acid, which are gradually extracted from a wood cask over the years. Below pH 7, the pH–charge curves for whisky were analogous to those for tannic acid, indicating that carboxyl groups in tannic acid were fairly stable on maturation of the whisky. The charge of the tannic acid increased with increasing pH, whereas that of whisky had a tendency to level off. The degree of leveling off was higher for whiskies with longer maturation. These phenomena are believed to be due to the oxidation of pyrogallol and catechol moieties in tannic acid, which occurs during storage of the whisky. There was a clear tendency for the whiskies with higher prices to have higher charges, that is, a higher tannic acid content.

Key words Whisky · Wood cask · Polyphenol · Tannic acid · Polyelectrolyte titration

Introduction

The concentration of ethanol in whisky is about 40%. Aqueous ethanol, which consists of 60% water and 40% absolute ethanol, is not good to drink because it is highly irritating to the tongue. Maturation in a wood cask is an indispensable condition for whisky, which is completely different from gin and vodka, which do not undergo maturation in a cask. It has been pointed out that the taste of whisky is attributable to the cluster between ethanol and water formed during maturation in the cask over several years.[1] The cluster is postulated to stabilize several components and their oxidation products, which are little by little extracted from the cask (usually made of white oak). It is known that the permittivity of whisky and the partial pressure of ethanol decrease with increased maturation, and these phenomena take place through the association of ethanol.[2]

The materials extracted from the wood cask into whisky are mainly sugar components and polyphenols, together with minor components such as coloring materials, lignin, amino acids, and minerals. Sato et al. has reported on the sugar components[3,4] and the changes of sugars, tannins, and taste during a 3-year maturation.[5]

Polyelectrolyte titration[6,7] using a fluorescent indicator, introduced in recent years, can analyze samples with low charge density, such as commercial cationic starches; the conventional method[8–10] using a metachromatic color change indicator, toluidine blue (TB), is inapplicable for such samples because of the unclear color change of TB at the endpoint. In the present study, polyelectrolyte titration[6,7] was applied to analyze various whiskies that contain polyphenols (e.g., tannic acid) as the major titrating anionic compounds to determine the relation between the amount of polyphenols and the degree of maturation.

Materials and methods

Six domestic whiskies and four Scotch whiskies were purchased at a liquor store. Their brand names are listed in Table 1. The tannic acid, potassium 6-(*p*-toluidino)-2-naphthalenesulfonate (TNS), polydiallyldimethylammonium chloride (PDADMAC), and other chemicals used were reagent grade.

A suitable amount (5–20 ml) of whisky was diluted to 100 ml with deionized water, and 5 ml of this solution was pipetted into a 50-ml beaker followed by addition of about 30 ml of water and a small amount of dilute aqueous HCl or NaOH to adjust and the pH. After addition of 2 drops of 0.1% TNS, this sample was titrated with 10^{-4}N

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Table 1. Brand names of whisky used

Code	Whisky
A	Suntory Red
B	Black Nikka
C	Suntory Old
D	Nikka All Malt
E	Johnnie Walker Red
F	Suntory Kioke
G	Johnnie Walker Black
H	Suntory Yamazaki
I	Glenfiddich
J	Royal Stirling

PDADMAC.[6] An aqueous solution of tannic acid (0.35 g/l) was titrated in a similar manner. Immediately after each titration, the pH of the resultant solution was measured. The fluorescence intensity during titration was automatically recorded using a spectrophotometer (Hitachi F3010) equipped with a small magnetic stirrer and an autoburette (Metrohm 665 Dosimat). The concentrations of the whiskies were adjusted so about 5 ml of 10^{-4}N standard PDADMAC would be consumed at the endpoint.

Results and discussion

Titration curve

Figure 1 shows the relation between pH and the electrolyte concentration (amount of charge) in Nikka All Malt whisky determined by polyelectrolyte titration. A concentration of 0.55 mEq/l at pH 3.5 is believed to originate mainly from the carboxyl groups of tannic acid and a little from hemicellulose. The charge increased with increasing pH in an S-shaped curve, suggesting the existence of polyphenols.

Because the main components of polyphenols, assumed to be tannic acid and tannins in whisky, were reported[5] to increase rapidly after the third year of maturation, the aqueous tannic acid was titrated at various pH levels in a similar manner. The results are shown in Fig. 2, together with those for All Malt and Suntory Yamazaki whiskies.

The curves indicating the relation between pH and charge are similar for tannic acid and the whiskies below pH 7. The result implies that whiskies contain a considerable amount of tannic acid, which they have extracted from the wooden cask. At alkaline pH the contribution of polyphenols, mainly tannic acid, to the charge is enhanced as the pH increases.

Figure 2 shows that the charge of tannic acid increased markedly at alkaline pH, but those of the whiskies had a tendency to level off. The tannic acid contains phenol, catechol, and pyrogallol moieties; and it is well known that tannic acid and gallic acid are powerful reducing agents for metallic ions such as $AuCl_3$, $AgNO_3$, and $Hg(CH_3CO_2)_2$ and are used as antioxidants for foods because the catechol and pyrogallol moieties are easily oxidized.

The leveling off phenomenon of the charge in whisky at alkaline pH might depend on the oxidation of catechol and

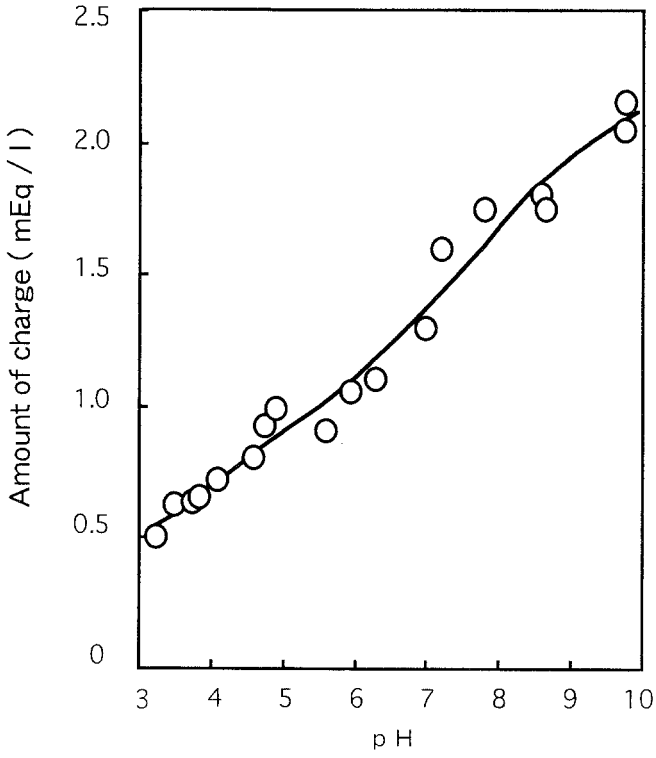

Fig. 1. Effect of pH on the concentration (charge) of Nikka All Malt whisky (D in Table 1)

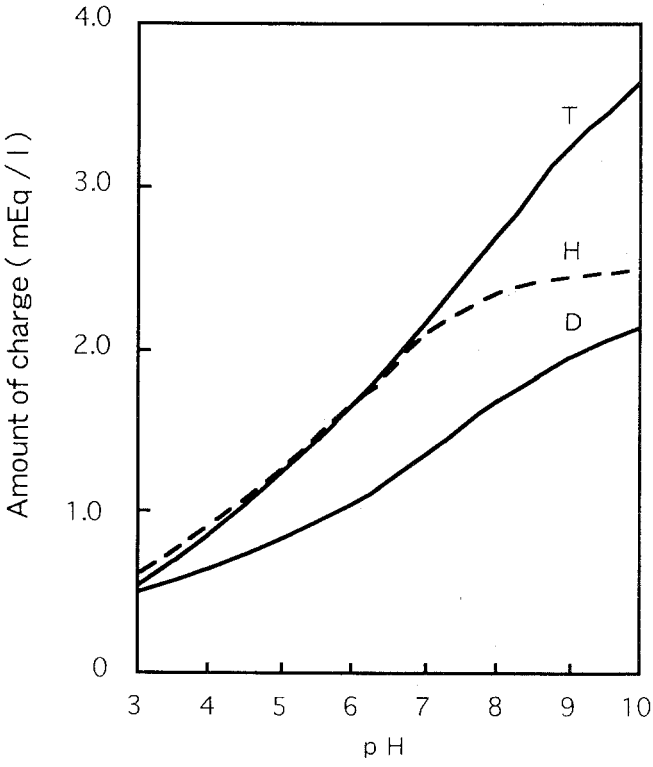

Fig. 2. Comparison of Nikka All Malt (*D*), Suntory Yamazaki (*H*), and tannic acid (*T*) relative to pH and charge

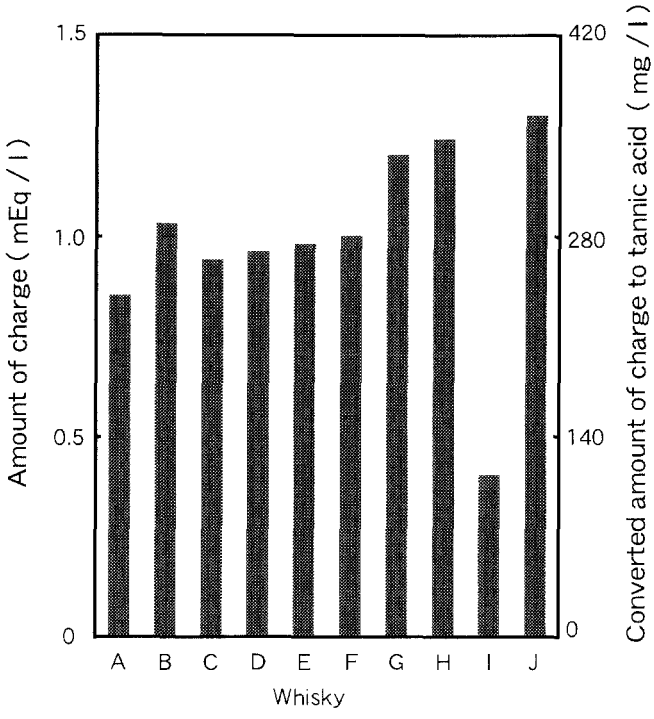

Fig. 3. Charge and converted charges to tannic acid of 10 whiskies at pH 5. *A*, Suntory Red; *B*, Black Nikka; *C*, Suntory Old; *D*, Nikka All Malt; *E*, Johnnie Walker Red; *F*, Suntory Kioke; *G*, Johnnie Walker Black; *H*, Suntory Yamazaki; *I*, Glenfiddich; *J*, Royal Stirling

pyrogallol moieties in tannic acid during long-standing maturation. Similarly, Sato et al.[5] noted that gallic acid originating from tannin might be altered to *o*-quinone by oxidation in air. Thus it must be interesting to compare the behaviors of Nikka All Malt whisky with those of Suntory Yamazaki whisky. The charge in All Malt is less than that in Yamazaki, but the increasing rate of charge at alkaline pH is higher. Because the maturation period of All Malt is not long (so the oxidation does not proceed to a large extent), a relatively large quantity of catechol and pyrogallol moieties may remain in the whisky. On the other hand, Yamazaki, which is expected to be matured much longer, has a higher charge than All Malt, but it does not increase much at alkaline pH because of the decreased amount of polyphenolic groups due to oxidation.

Polyelectrolyte titration of various whiskies

The pH of whisky is usually around 5.0. Thus the polyelectrolyte titration was carried out at pH 5 for six domestic whiskies and four Scotch whiskies. Results are shown in Fig. 3, together with the converted amount of charge to tannic acid.

The converted charges to tannic acid were about 270 mg/l for whiskies B–E, the prices of which were lower than 3000 yen, though that of the least expensive one (A) was 240 mg/l. Figure 3 indicates that the tannic acid content in whisky increases with increasing prices, that is, with the increasing period of maturation, except for whisky I (Glenfiddich). The tannic acid content in Glenfiddich was exceptionally low. This whisky has a light brown color, which may be due to the low tannic acid content, but the details are not clear at the moment.

As described earlier, whiskies with longer maturation have the lowest ratio of charges determined at pH 10 compared to that at pH 7. It would be interesting to compare these ratios for whiskies with various periods of maturation, and these experiments are currently under way.

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